

SMP044-01

Room:301B

Time:May 25 10:00-10:15

muSR study on the behavior of trace hydrogen in silicates

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Hydrogen is the most abundant element in the solar system and the presence of water, which is formed by binding hydrogen and oxygen, makes the Earth a habitable blue planet. It is also believed that the presence of water, even if its amount is very small, alters physical and chemical properties of silicates significantly (for example, depression of melting temperature, decrease in viscosity, increase in electrical conductivity, etc.) and therefore plays an important role in geodynamics such as igneous activity and mantle convection and, what is more, in the terrestrial evolution from past to present to future.

That is why "water (hydroxyl)" in silicates has attracted a lot of interest and so far been studied by many researchers. On the other hand, "isolated hydrogen" in silicates may have been overlooked in previous studies because it is hard to probe the behavior of isolated hydrogen with ordinary techniques used in mineral physics and crystal chemistry. In the field of semiconductor science, however, it is well known that eliminating isolated-hydrogen atoms from a semiconductor is quite difficult and that their presence has remarkable effects on its physical properties. In the broad sense, silicates are classified as a semiconductor (i.e., wide-gap semiconductor) and therefore it may be possible that the same scenario takes place in them. The purpose of this study is to clarify the behavior of "isolated hydrogen" and "water" in silicates with muon spin rotation/relaxation/resonance (muSR) techniques, which have worked well in studies on "isolated hydrogen" in semiconductors.

Muon is a particle having a mass about 9 times less than that of proton and a spin of 1/2. In certain materials, a positive muon can pick up an electron to form a hydrogen-like atom called muonium. Therefore, positive muon can be considered to be a lighter version of proton. In muSR measurements, information about the site, the electronic state, and the diffusion dynamics of muon (an isotope of proton) can be obtained, by measuring the time evolution of the spin polarization of the muon implanted into a sample. Neutron diffraction is also a powerful tool to probe the behavior of hydrogen in materials. However, in neutron diffraction measurements, hydrogen should be in a framework structure of materials. muSR has the advantage of being able to probe the behavior of trace hydrogen irregularly located in interstitial sites of materials.

Japan Proton Accelerator Research Complex (J-PARC, Tokai-mura, Japan) is now successful in producing the most intense pulsed-muon beam in the world. The intense beam makes it possible to conduct muSR measurements on a relatively small sample (approximately 15 mm in diameter and 1 mm in thickness) at Materials and Life Science Experimental Facility (MLF). We applied to non-proprietary use experiments at MLF to clarify the effect of microscopic structures of silicates on the behavior of trace hydrogen and have the first beamtime in March 2011. In the first beamtime, we will conduct muSR measurements on high-pressure crystalline and glassy phases of SiO₂ at ambient pressure. The samples have been prepared by using a belt-type high-pressure apparatus at National Institute for Materials Science (NIMS). In the future, we plan to develop high-pressure in-situ muSR techniques to conduct experiments at the conditions of the Earth's Interior. At the meeting, we will report about the first beamtime and discuss our plan to use muSR techniques in Earth science.

SMP044-02

Room:301B

Time:May 25 10:15-10:30

High pressure form of AlPO_4 with moganite structure

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We recently found three high-pressure phases of AlPO_4 , and structural and NMR spectroscopic study of two phases (P-1, P21/c phases) are reported (Kanzaki et al., *Acta Cryst. B*, 2011). Third phase (synthesized at 5 GPa and 1500 °C) is later found to have moganite-type structure. Although moganite-type phase is reported for "PON" at high pressure, this is first moganite phase found in ABO_4 system.

AlPO_4 moganite was found in the sample recovered from 5 GPa and 1500 °C synthesized at SPring-8 using SPEED 1500 press. Micro-Raman spectroscopic inspection of the sample revealed the phase is previously unknown phase. ³¹P MAS NMR and ²⁷Al 3Q MAS NMR indicate two tetrahedral sites for both Al and P, with intensity ratio 2:1. Powder X-ray diffraction of the sample is obtained by Rigaku's SmartLab. Since originally the structure was unknown to us, the structure was solved by FOX using XRD pattern with help of NMR information, and refined by Rietveld method (RIETAN-FP). The structure can be regarded as an ordered replacement of Si in moganite with Al and P, like berlinite. As a result, the space group of the phase is P2/c (moganite SiO_2 and PON are I2/a). First-principles calculation of the phase confirmed its structural stability. First-principles NMR properties calculations using GIPAW method were conducted, and the calculated parameters for moganite phase are consistent with those observed ³¹P and ²⁷Al NMR.

The phase was also observed in in-situ high T-P powder X-ray diffraction measurements at BL04B1, SPring-8. Moganite phase stabilizes at 4 GPa from berlinite. Moganite phase transforms to AlVO_4 (P-1) phase at 6 GPa and below 1250 °C, but at 6 GPa and above 1250 °C transforms to P21/c phase. Contrast to this, no moganite stability field was known for SiO_2 to date. Moganite phase was also reported in PON from high-pressure runs, but moganite phase was low pressure form of quartz phase (Chateau et al., *Am. Mineral.*, 1999). Therefore, pressure-induced phase transformation sequence is opposite between AlPO_4 and PON. Differences of enthalpy and volume of quartz and moganite is small, thus these properties might be reversed with chemistry.

Temperature-induced displacive phase transformation for SiO_2 moganite was reported (Heaney & Post, *Am. Mineral.*, 2001), similar to those of quartz and cristobalite. Thus, such transition might be expected for AlPO_4 moganite. We are planning high-T Raman study to confirm this transition, and will report at the meeting.

To date, no synthesis condition for SiO_2 moganite is known, and only natural samples with low crystallinity and coexisting other phases have been used for research. AlPO_4 moganite can be synthesized, and thus can be used for study to understand behavior of moganite structure.

Keywords: moganite, AlPO_4 , high pressure, phase transformation, crystal structure

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SMP044-03

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Theoretical and experimental evidence on the post-cotunnite phase transition in dioxides

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The cotunnite-type structure is identified as the highest-pressure phase in many dioxides and the post-cotunnite phase was still underdetermined. However, very recently, an *ab initio* work on silica has demonstrated a new possible phase transition to an unexpected hexagonal Fe₂P-type structure at 690 GPa with skipping the cotunnite-type stability at the static temperature (T. Tsuchiya and J. Tsuchiya, Proc. Natl. Acad. Sci. U.S.A. **108**, 1252, 2011). In this study, we systematically examined possible post-cotunnite phase transitions in several low-pressure analogs of silica, GeO₂, SnO₂, TiO₂, and ZrO₂, with the electronic and crystallographic properties. Based on the theoretical prediction, we have performed in situ LH-DAC experiments and succeeded in experimental synthesis of the Fe₂P-type post-cotunnite phase in TiO₂.

Research supported by Senior Research Fellow Center, Ehime University.

Keywords: first principles calculation, high pressure, post-cotunnite phase transition, dioxide

SMP044-04

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Development of density measurement method using X-ray micro tomography under pressure

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Density of melt is an important property for discussing melts related geodynamics processes in the deep Earth. Density measurement of melt at high-pressure is challenging because of its technical difficulties. Several methods, such as sink-float and the shock experiments have been developed to measure the densities of melts, but they are not enough. We have developed the novel X-ray absorption technique to measure the densities of melts at the desired P-T conditions using the multi-anvil press and synchrotron radiation. However, it has an intrinsic uncertainty because the length of sample is not measured directly. X-ray tomography is a breakthrough technique, which can yields the sample length as well as the sample absorption for X-ray. Thus, we are developing the new density measurement technique for melts using the high-pressure X-ray micro-tomography. Here we report the results of the reconnaissance experiments using the polycrystalline KBr up to 3 GPa.

X-ray tomography experiments were carried out using the tomography press TPH at BL20B2, SPring-8. The TPH is the 80 tons uniaxial press with two wide windows for observation and equips the toroidal type opposed-anvils. The TPH was set on the X-Y-Z-rotating stage and X-ray shadowgraphs of sample were acquired each 0.2 degree during rotation of the TPH. X-ray absorption of sample (I/I_0) was calculated from the shadowgraph image, and the sample length t was evaluated using the tomography slice image. Then, the densities of KBr at high pressures were calculated based on the Lambert-Beer law. The mass absorption coefficient of KBr was evaluated from the data acquired at 0.1 MPa, where the density is well defined.

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SMP044-05

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Simultaneous measurements of density and elastic wave velocities of NaCl at high pressures: absolute pressure scale

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The elastic compressional and shear wave velocities and densities of NaCl at 300 K and high pressures were measured using a combination of ultrasonic interferometry, in situ synchrotron X-ray diffraction and radiographic techniques in a large-volume Kawai-type multi-anvil apparatus. We adopted experimental data after heating the sample to 773 - 873 K under fixed press loads, to minimize nonhydrostatic components due to local deviatoric stresses, and have obtained high-quality elastic wave velocity and density data up to 12 GPa at 300 K. Both compressional and shear wave velocities are found to change linearly with density up to 12 GPa, satisfying Birch's law. Based on these measured data, we have derived the P-V equation of state (EOS) of NaCl at 300 K independent of any pressure scale. Comparison of the 300 K EOS between the present and previous studies will be presented in detail.

Keywords: pressure scale, NaCl, elastic wave velocity, high pressure

SMP044-06

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Thermodynamic properties of stishovite by heat capacity measurements and the coesite-stishovite transition boundary

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Stishovite is one of important minerals in science of the earth's mantle, and the coesite-stishovite transition boundary is widely used for pressure calibration at high temperature. The low-temperature isobaric heat capacity (C_p) of stishovite synthesized at 15.5GPa and 1400°C was measured between 2.3 and 311.4 K by thermal relaxation method using a PPMS. The measured C_p was considerably smaller than that by Holm et al. (1967) in the whole temperature range studied. The standard entropy, S_{0298} , of stishovite obtained is 24.0 J/mol.K, which is 3.8 J/molK smaller than that by Holm et al. (1967). Using the measured C_p , Debye temperature and thermal Gruneisen parameter at 298 K were calculated to be 1109 K and 1.68, respectively. The equilibrium coesite-stishovite transition boundary was calculated using the S_{0298} of stishovite with published thermodynamic data including enthalpy of transition by Akaogi et al. (1995). The calculated boundary has a slope of 3.2 ± 0.1 MPa/K at 1200-1600 K which is larger than the slope determined by high-pressure in situ X-ray diffraction study by Zhang et al. (1996).

Keywords: stishovite, thermodynamic property, heat capacity, coesite-stishovite transition

SMP044-07

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High-pressure Raman spectroscopy of calcium ferrite-type MgAl_2O_4

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A calcium ferrite phase appears as a high-pressure phase in the basalt under lower mantle conditions. Calcium ferrite-type MgAl_2O_4 is one of the major endmembers of the calcium ferrite phase. It is considerably difficult to synthesize a large amount of calcium ferrite-type MgAl_2O_4 because it is stable at pressures higher than 25 GPa. This prevents calorimetric measurements for the determination of its enthalpy, entropy and heat capacity, which are needed to discuss the thermodynamic stability. In this study, the thermal Grueneisen parameter used to calculate theoretically the isobaric heat capacity (C_p) was determined by performing high-pressure Raman spectroscopy.

A sample for the Raman spectroscopy was synthesized by keeping a starting sample of MgAl_2O_4 spinel at 27 GPa and 2200 C for 1 hour using a Kawai-type multi-anvil high-pressure apparatus. Micro-Raman spectroscopy was done using JASCO NRS-3100 (Nd:YAG laser with 532 nm). Observed Raman shifts were calibrated by those of trichloroethylene. A small chip of the sample was compressed using a diamond anvil cell high-pressure apparatus at ambient temperature. The pressure medium and metal gasket used were a mixture of methanol:ethanol = 4:1 (in volume) and SUS304 with 0.25 mm thickness, respectively. Pressure was determined by the ruby R_1 line.

Frequency changes for eighteen Raman-active lattice vibrational modes with increasing pressure at ambient temperature were observed in the pressure range from 1 atm to 10 GPa, at which the pressure medium is solidified. Mode Grueneisen parameters were calculated using lattice vibrational frequencies at 1 atm, pressure dependences of the frequencies, bulk modulus (K_T) of 241 GPa by Yutani et al. (1997). We obtained mode Grueneisen parameters of 1.07-2.67. The weighted average of them gave the thermal Grueneisen parameter of 1.67(4) by considering the contribution of heat capacity at constant volume (C_v) for each vibrational mode to total one, C_{v_i}/C_v . The C_{v_i} was calculated from the Einstein function. The obtained thermal Grueneisen parameter of calcium ferrite-type MgAl_2O_4 is slightly larger than that of calcium ferrite-type CaAl_2O_4 which was determined as 1.52(2) using the same method. This difference is caused by larger pressure dependencies of vibrational frequencies distributing in the range of 200-300 cm^{-1} for calcium ferrite-type MgAl_2O_4 than for calcium ferrite-type CaAl_2O_4 . The vibrational modes in this region consist mainly of stretching modes of divalent cation (Mg^{2+} or Ca^{2+}). Therefore, it is implied that the lattice vibrations of divalent cations relatively affect the Grueneisen parameters in the calcium ferrite-type crystal structure.

Keywords: calcium ferrite, Raman spectroscopy, High-pressure, lattice vibration, Grueneisen parameter

SMP044-08

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Comparison in temperature dependence of Ti K edge XAFS spectrum for PbTiO₃,PZT, ATiO₃ compounds (A=Mg,Ca,Sr,)

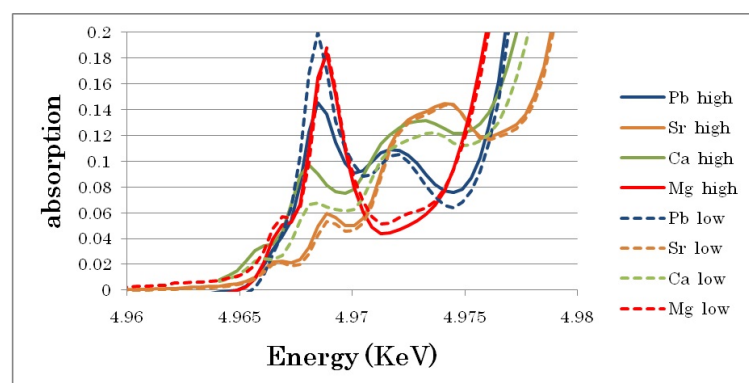
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Ti k-edge X-ray absorption near edge structure (XANES) spectra of PbTiO₃ and various titanates such as ATiO₃ (perovskite- and ilmenite-type structure, A=Mg,Ca,Sr,Ba,) were measured at various temperatures up to 1100 K. The composition, local structure and temperature dependence of XANES spectra was investigated especially on the phase transition. Ti atoms are located in TiO₆ octahedral sites for the all samples. Ti k-edge XANES spectra change largely with different compositions, while the temperature dependence of XANES spectra is small in the each compound even if undergoing structural phase transition. Perovskite-type ATiO₃ compounds reveal several phase transitions. SrTiO₃ and PbTiO₃ perovskite undergo structural phase transition in the temperature ranges in this study, SrTiO₃; rhombohedral-tetragonal-cubic, PbTiO₃; tetragonal-cubic, weak but distinct changing of the XANES spectra was observed near phase transition point. These structural transitions of perovskite are caused mainly by rotation and distortion of TiO₆ octahedron. Pre-edge feature and local structure around Ti atom is little changing by rotation of octahedron. The distinct changing of pre-edge XANES spectra was observed at some transition points. Five pre-edge peaks can be identified: pp(a) 4.9667eV, pp(b) 4.9687eV, pp(c) 4.9727eV, pp(d) 4.9747eV and pp(e) 4.9796eV. The temperature dependence for each pre-edge peaks is largely different in temperature and local structure [1]. The different behaviors of the pre-edge intensity suggest that the increase and decrease of X-ray absorptivity at various temperatures is fluctuated by the hybridized orbital proportion and local symmetry.

References

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Keywords: perovskite, ferroelectric, phase transition

SMP044-09

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Variety of Ti local structure in Tektite

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Tektite is formed as the meteorite impact the earth surface. Mass extinction is thought the reason of impact event, which is dated to 65 Ma. What happened at the event? According to research of tektite, speculate process of the event. Local structures of Sb, Zn in K-T clay are studied. Local structure of Ti in tektite is studied by X-ray Absorption Fine Structure (XAFS) method. XAFS is an advanced method, which can get detail information of valance state, neighboring atoms and the coordinated state. Local structures of Ti in tektites form different strewn fields are compared. The thresholds of XANES spectrum in various tektites are the same. They are also the same with nature minerals, which is Ti 4+. The intensity of pre-edge in moldavite is smaller than other tektites. But the previous studied by Farges, F. is shown the pre-edge intensity of Moldavite is strong as another tektite, and the coordination number is considered to four. According to the Fourier transformation spectrum are divided in three kinds. The Hainantite, Indochinite, Bediasite; Australite, Philippinite and the Moldavite; the Ti-O distance becomes large in proper order by each group. Coordination numbers and radial structure function determined by EXAFS analyses, we classified the tektites in three types: in Hainanite, Indochinite and Bediasite, Ti occupy 4-fold coordinated tetrahedral site and Ti-O distances are 1.84-1.79 Å; in Australite and Philippinite, Ti occupy 5-fold trigonal bi-pyramidal or tetragonal pyramidal site and Ti-O distances are 1.92-1.89 Å; in Moldavite, Ti occupy the 6-fold octahedral site and Ti-O distance is 2.00-1.96 Å. Ti occupies the TiO₆ octahedral site in many titanium minerals at ambient conditions. This study indicates that the local structure of Ti may be changed in the impact event and the following stage. Tektites splash to the space and travel in several kinds of processes and routes, which lead to different temperature and pressure history. Local structure of Ti should be related with the temperature, pressure, quenching rate, sizes of impact meteorite and size of falling melts. As a result, there are some differences in the bonding structure of Ti atoms and arrangements of neighbouring oxygen.

Keywords: local structure, titanium, tektite, XAFS

SMP044-10

Room:301B

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Seebeck Coefficient of Gabbro under Non-uniform Stress

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When a terminal of an air-dried igneous rock block is uniaxially loaded to form the non-uniform stress in the block at a room temperature, there appears the electromotive force that makes electric current flow from the stressed volume to the unstressed volume. Quartz-free gabbro tends to generate the stronger electromotive force than quartz-rich granite. Therefore, it is inconsistent to consider piezo-electric effect as the cause of this electromotive force. To explain this force, we have expected that positive charge carriers (holes) are generated in the stressed volume and flow into the unstressed volume. This will be the source of the electromotive force induced by non-uniform stress. However, we do not yet obtain reliable evidence for the activation/spread of positive holes. In this study, we measured thermoelectromotive force of air-dried gabbro blocks whose one terminal was uniaxially loaded/unloaded. We verified the activation/spread of positive holes from the increase/decrease of the Seebeck coefficient during loading/unloading. The hotter temperature was about 150 deg. C., the colder was about 30 deg. C., and the temperature difference was about 120 deg. C. The results indicated that the Seebeck coefficient of the gabbro without loading was about 0.8-1.2mV/K, meaning the majority of charge carriers are hole. On the other hand, the Seebeck coefficient of the volume under 60MPa of stress decreased to about 0.5-0.7mV/K, and that of the volume under stress free did not remarkably change. This meant that the concentration of holes increased in the stressed volume and such a change was little in the unstressed volume. In conclusion, it was clarified that holes were activated in the stressed volume and the distribution of the holes spreading reached only near around the stressed volume. As the source of the holes, we have focused on peroxy bonds, one of the most popular lattice defects in igneous rock-forming minerals, e.g., $O_3Si-OO-SiO_3$ in quartz. When this bond is deformed by mechanical force, an antibonding energy level of this bond shifts down into the Valence band and an electron can jump in this level from a neighbor oxygen site. As a result, a positive hole is activated in this neighbor site and an electron is trapped in the deformed peroxy bond. Once positive holes are activated, they can spread away through the Valence band. Provably, only a little part of the positive holes reached the unstressed edge. The slant in the distribution between these positive holes and the electrons trapped at the deformed peroxy bonds, i.e., the electric polarization in the stressed volume, is the source of the electromotive force induced by non-uniform loading.

Keywords: Igneous rock, Electromotive force, Seebeck coefficient, Lattice defect, Positive hole

SMP044-P01

Room:Convention Hall

Time:May 25 14:00-16:30

Synthesis of polycrystalline sintered stishovite and its physical property measurements

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We synthesized polycrystalline sintered stishovite at pressure of 15 GPa and temperature of 1473 K. The starting material was a silica glass rod with diameter of 2.5 mm and height of 2.7 mm in. This was enclosed in a platinum capsule. The recovered sample was a whitish translucent rod with diameter of about 2 mm and height of about 2.3 mm. The recovered sample was examined by micro-focused X-ray diffraction and micro-Raman spectroscopic measurements. The results indicate that the recovered sample is a pure polycrystalline stishovite. Ultrasonic measurements were carried out at ambient conditions. We determined compressional wave velocity of 11.776 km/s and shear wave velocity of 7.174 km/s. We measured bulk density of this sintered stishovite by Archimedian method. The density is 4.282 g/cm³. Using these parameters, we calculated elastic moduli of this sample: Bulk modulus, 300 GPa; shear modulus, 220 GPa; Youngs modulus, 531 GPa; Poissons ratio, 0.204. These values are consistent with those obtained by previous studies. We have also conducted X-ray diffraction measurements under low and high temperature between 90 and 1000 K at BL02B2, SPring-8. We are going to report temperature dependence of thermal expansivity of stishovite in the session.

Keywords: stishovite, sintered polycrystalline sample, elastic wave velocity, thermal expansivity

SMP044-P02

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Anomalous behavior of low-density SiO₂ in helium under high pressure

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Properties of SiO₂ crystals and glass are one of the most classical and important issues in Earth science. Numerous studies on the high-pressure behavior of these materials have been conducted because of their importance not only in Earth science but also in materials science and condensed-matter physics. It is well known that SiO₂ crystals, such as cristobalite, tridymite, and quartz, and the glass obtained at ambient pressure have three-dimensional network structures consisting of SiO₄ tetrahedra. Considering the fact that the density of quartz is 2.65 g/cm³ (at ambient pressure) and that of stishovite is 4.29 g/cm³, it can be assumed that fourfold-coordinated structures contain a large amount of voids. If small gas molecules such as helium and hydrogen dissolve in these voids, it is expected that the compressional behavior of these materials may be changed and/or new structures may appear. In this presentation, we will report anomalous behavior of SiO₂ glass and cristobalite, fourfold-coordinated SiO₂ having especially low densities (2.20 and 2.33 g/cm³, respectively), in helium at high pressures. All experiments were conducted using a diamond-anvil cell.

The pressure dependence of the volume of SiO₂ glass was determined by measuring the change in the size of the bulk sample in microscope images [Meade & Jeanloz, 1987]. The result up to 10 GPa shows that the volume change of SiO₂ glass in a helium medium is much smaller than in a mixture of methanol-ethanol medium, suggesting that the voids in SiO₂ glass are prevented from contracting because a large amount of helium penetrates into these voids. The solubility of helium in SiO₂ glass is estimated to be more than 1 mol per mole of SiO₂ glass at 10 GPa. X-ray diffraction measurements also show that the pressure-induced shift of the position of the first sharp diffraction peak (FSDP) in helium is significantly smaller than that in previous studies. The FSDP is associated with the presence of the intermediate-range order and considered to arise from the periodicity of ordering of the rings consisting of SiO₄ tetrahedra [Elliott, 1991; Mei et al., 2008]. Therefore this small shift of the FSDP is consistent with the small volume change. The result of Raman scattering measurements is also significantly different from those in the previous studies with argon and other mediums.

On cristobalite, x-ray diffraction measurements were conducted. At around 10 GPa, a new phase, which has diffraction peaks at larger *d* values, was observed. It may be possible that the volume increases as helium dissolves in cristobalite. Above 20 GPa, another new phase, which has very broad diffraction peaks, was observed. At this pressure range, the transformation to a stishovite-like structure was observed in argon and other mediums [Yamakata and Yagi, 1997]. This second new phase might have a sixfold-coordinated structure. We are planning to obtain more precise data in order to determine the structures of these two new phases.

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SMP044-P03

Room:Convention Hall

Time:May 25 14:00-16:30

High-pressure X-ray diffraction and Raman spectroscopic studies of magnetite, ulvospinel, and chromite

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Magnetite Fe_3O_4 , ulvospinel Fe_2TiO_4 , and chromite FeCr_2O_4 have been investigated by high-pressure x-ray diffraction and Raman spectroscopy with diamond anvil cell techniques. The crystals used as starting materials were synthesized in a 1-atm furnace at 1100 °C for 48 hours with a CO/CO_2 gas flow from dried powdered oxides of Fe, Ti and Cr. A powder x-ray diffraction study of magnetite was performed up to 154 GPa with and without laser heating. The x-ray diffraction profiles showed changes at 28 GPa. With further compression up to 154 GPa, a phase change occurred above 80 GPa. Powder x-ray diffraction measurements of ulvospinel were carried out up to 60 GPa at ambient temperature. Phase transitions in ulvospinel were found near 9 GPa, 12 GPa, and 50 GPa, respectively where the crystal structure transforms from cubic to orthorhombic through a tetragonal phase. The phase observed above 50 GPa was reversibly changed to the lower-pressure phase with decompression. The x-ray diffraction profile above 50 GPa can be explained by the high pressure phase of the CaTi_2O_4 type structure (space group $Cmcm$) with lattice parameters $a = 2.65$, $b = 9.25$, $c = 9.30$ Å, and $V = 228$ Å³. Structural refinements of chromite were obtained from single-crystal x-ray diffraction measurements collected at several pressures up to 15 GPa. A phase transition in chromite was found at 12 GPa. The crystal structure of chromite transforms from cubic to tetragonal in a manner similar to the pressure induced phase transitions in ulvospinel. Fitting of the P-V data to a Birch-Murnaghan equation of state (EoS) results in $K_0 = 196(5)$ GPa, $K' = 4.0$ (fixed), and $V_0 = 589.2(1)$ Å³. The K_0 value for chromite is in fair agreement with the experimental results of spinels and theoretical predictions of chromium spinels. From the structural refinements the tetrahedral site (T) is occupied by Fe^{2+} cation with a greater compressibility than the octahedral site (M) occupied by the Cr^{4+} cation owing to the Jahn-Teller effect at Fe^{2+} . The resulting EoS parameters for the T-site and M-site are $K_0 = 141(3)$ GPa, $K' = 4.0$ (fixed), $V_0 = 4.1(1)$ Å³ and $K_0 = 256(9)$ GPa, $K' = 4.0$ (fixed), $V_0 = 10.4(1)$ Å³, respectively.

The three spinels were studied by laser Raman spectroscopy using a laser power of the 532 nm laser line of 1-2 mW on the sample. There are five Raman-active modes ($A_{1g} + E_g + 3F_{2g}$) in the $Fd-3m$ space group of the cubic spinel according. Two Raman active modes assigned to A_{1g} and F_{2g} are clearly observed around 500 and 700 cm^{-1} under ambient conditions. The A_{1g} mode in the cubic structure transforms to the A_g mode in the tetragonal and orthorhombic structures. In contrast, the F_{2g} mode in the cubic structure splits into $B_{1g} + E_g$ modes in the tetragonal structure, and then into $B_{1g} + B_{2g} + B_{3g}$ modes in the orthorhombic structure. With increasing pressure, in the Raman spectra of chromite, the A_{1g} and F_{2g} modes in chromite do not change up to 20 GPa except for a continuous shift to higher frequencies. The Raman spectra of ulvospinel and magnetite start to broaden gradually with increasing pressure. It seems reasonable to attribute the observed broadening to the peak splitting caused by the structural phase transitions. The most striking characteristic of the Raman spectrum of ulvospinel is that compression leads to the extinction of the Raman active mode derived from F_{2g} symmetry. The F_{2g} mode in ulvospinel disappears completely at 20 GPa, but its A_{1g} mode can be observed continuously up to 57 GPa. The Raman spectra of both A_{1g} and F_{2g} modes in magnetite disappear at 30 GPa.

Keywords: magnetite, ulvospinel, chromite, phase transition, high-pressure & high-temperature, diamond anvil cell

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Measurement of elastic constants of single-crystal chromian spinel by high frequency resonant ultrasound spectroscopy

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Chromian spinel found in mantle xenoliths contains fluid inclusions whose residual pressure (fluid density) can provide us the origin depth of the xenoliths. A host chromian spinel grain should have deformed in response to a change in ambient temperature and pressure during its transport, and changed the fluid density. Elastic and plastic properties of chromian spinel are essential for evaluation of the deformation and precise estimation of the origin depth. Although elastic constants of spinel (MgAl_2O_4) and chromite (FeCr_2O_4) have been already reported, few studies have been done on chromian spinel. We thus have studied elastic constants of a single-crystal chromian spinel using a resonance method. Chromian spinel crystals were collected from mantle xenoliths from Sveyagin, Russia (Yamamoto et al., 2009, Island Arc). One crystal was selected in terms of the uniformity of crystallographic orientation examined by SEM-EBSD. Each face was polished flat (< 1 micrometer) in an orientation parallel or perpendicular to $\{100\}$ by the X-ray precession method. The selected crystal was shaped into a rectangular parallelepiped ($0.412 \times 0.407 \times 0.497$ mm³). The Mg/(Mg+Fe(II)) ratio is 0.75, and the Cr/(Cr+Al) ratio 0.08. The density is 4.3×10^3 kg/m³. The resonant frequency was measured from 3 to 11 MHz using a system specially designed for such a small sample (Yoneda et al., 2007, JJAP). Preliminary analysis has shown that C_{11} , C_{12} , and C_{44} are 263.26, 137.96, and 123.71 (GPa), respectively. Comparison with elastic constants of spinel and chromite will be discussed in terms of the compositional difference.

Keywords: elastic constants, resonance method, chromian spinel

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High-pressure stability field and thermodynamic properties of anhydrous phase B (Mg₁₄Si₅O₂₄)

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Anhydrous phase B (Anh-B: Mg₁₄Si₅O₂₄) is a high-pressure magnesium silicate possibly stable in magnesium-rich regions in the upper mantle (Ganguly and Frost, 2006). They examined the equilibrium boundary of the reaction, 5forsterite (Fo) + 4periclase(Per) = Anh-B, at 9.0-12.5 GPa and 1173-1873 K. Ottonello et al. (2010) computed thermo-chemical and -physical properties of Anh-B by first principles calculation. However, those of Anh-B have been poorly determined by experiments. In this study, we examined stability field of Anh-B by high pressure experiments, and performed drop-solution calorimetry, heat capacity measurement and high temperature X-ray diffraction measurement on Anh-B. Obtained data were applied to thermodynamic calculation of the phase equilibrium boundaries of the reactions Fo+Per =Anh-B and Anh-B=Wads+Per which were separately determined by high pressure experiments.

High-pressure high-temperature phase relations experiments on Anh-B were performed using a Kawai-type 6-8 multianvil high pressure apparatus. The starting material was a mixture of Per and Fo with 4:5 in molar ratio. The experimental conditions were in a pressure range of 12-23GPa and in a temperature range of 1673 -2073 K. Samples recovered after quenching were analyzed with powder X-ray diffraction method and SEM-EDS. Drop solution calorimetry of Anh-B was performed using a Calvet-type calorimeter with Ar bubbling technique and lead borate solvent. Heat capacity was measured by DSC in a range of 300-770 K. High temperature X-ray diffraction measurements were made in a range of 303-773K every 50 K step. Raman spectroscopy of Anh-B was done using a micro-Raman spectrometer (JASCO NRS-3100).

The results of the high-pressure and high-temperature experiments indicated that the equilibrium boundaries of 5 Fo + 4 Per = Anh-B and of Anh-B = 5 Wadsleyite(Wads)+ 4 Per are located at 13 GPa and at 19 GPa, respectively, at 1873 K. The drop-solution enthalpy of Anh-B was determined to be 844.3 +/- 29.9 kJ/mol. The drop-solution enthalpy of Fo was 168.2 +/- 0.9 kJ/mol, and that of Per was 33.7 +/- 1.0 kJ/mol (H. Kojitani, unpublished data), and that of Wads was 142.2 +/- 2.7 kJ/mol (Akaogi et.al., 2007). The enthalpy changes for the reactions 5 Fo+ 4 Per = Anh-B and Anh-B = 5 Wads + 4 Per were obtained as 130.9 +/- 30.5 kJ/mol and -1.46 +/- 33.08 kJ/mol, respectively. We obtained a heat capacity equation of $C_{P(Anh-B)} = 1.531 \times 10^3 - 1.315 \times 10^4 T^{-0.5} - 7.925 \times 10^8 T^{-3}$ and thermal expansivity of $2.07 \times 10^{-5} + 1.75 \times 10^{-8} T$. Raman spectrum of Anh-B were consistent with lattice vibrational mode frequencies calculated by Ottonello et al. (2010). By applying the C_P , thermal expansivity and Raman data to Kieffer model calculation, entropy of Anh-B was estimated to be 563.37 J/(mol K). Therefore, entropy changes for the reactions 5 Fo+ 4 Per = Anh-B and Anh-B = 5 Wads + 4 Per were obtained as -14.43 kJ/(mol K), and -24.07 kJ/(mol K), respectively. The phase boundaries by thermodynamic calculations were consistent with those obtained by the high pressure experiments. It is concluded that stability field of Anh-B is placed at the range of 13-19 GPa and 1873 K.

Keywords: anhydrous phase B, high pressure high temperature experiment, thermodynamic calculation

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Thermal properties of hydrous minerals under pressure

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We measured thermal diffusivity, thermal conductivity and heat capacity of hydrous minerals, and found their particular behavior in the thermal property. Among hydrous minerals, serpentine ($\text{Mg}_6\text{Si}_4\text{O}_{10}(\text{OH})_8$) and talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$) are thought to be important, because their water exchange among major components, olivine or peridotite. Measurements were conducted using a pulse heating method in the Kawai apparatus. Antigorite has much lower thermal diffusivity and thermal conductivity (less than half) of the major dry mantle minerals such as olivine. The pressure derivative of thermal diffusivity or thermal conductivity is small compared with olivine. On the other hand, talc has relatively higher thermal conductivity compared with antigorite. Antigorite and talc are quite similar hydrous sheet minerals. Although talc, one of the softest mineral, has lower acoustic velocity than antigorite, thermal conductivity of talc is two to three times greater than that of antigorite. This apparent contradiction may be attributed to alternating wavy structure in antigorite with a few nanometer wave length. In terms of a simple calculation, phonons excited at 300 K tend to have wavelengths shorter than 1 nm. Therefore, phonons may be trapped in a wavy segment of the antigorite crystal structure. This can cause lower thermal conductivity for antigorite. Heat capacity is obtained from the simultaneous measurement of thermal diffusivity and thermal conductivity. The heat capacity of antigorite at ambient temperature is ca. $1.0 \times 10^3 \text{ Jkg}^{-1}\text{K}^{-1}$ and nearly independent of pressure increase, that is, the pressure derivative of heat capacity of antigorite is nearly zero. This value contrasts with the negative value for olivine. On the other hand, preliminary results for talc showed the positive pressure derivative. From the pressure derivatives of heat capacity, we can evaluate characteristics of the thermal expansivity. We can expect nearly constant thermal expansivity for antigorite for some assumptions. In other words, the volume of antigorite increases almost linearly with temperature. From lattice dynamic theory, we can define the mode Grueneisen parameter for the normal mode of lattice vibration. Note that the positive parameter contributes to positive thermal expansion, and vice versa. Thus, the majority of the parameter for olivine is expected to be positive. On the other hand, some of the parameter for antigorite and talc are expected to be negative. It is quite probable that the hydrous mode, or normal mode related with hydrogen and hydroxyl groups, may have a negative mode Grueneisen parameter. Thus, hydrous minerals reveal particular thermal properties and its behavior is different from major mantle minerals such as olivine.

Keywords: thermal diffusivity, thermal conductivity, heat capacity, high-pressure, hydrous mineral

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Equation of state of antigorite at high pressure and temperature

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Antigorite plays key roles in subduction zone processes including transport of water and seismogenesis. The equation of state (EoS) of antigorite is critical for understanding of its stability field and for interpretation of seismological observations. Although a few compression tests have been conducted at room temperature, EoS is still poorly understood at high temperatures. We have investigated EoS of antigorite by in-situ synchrotron X-ray powder diffraction. Measurements were conducted at a beamline NE5C of Photon Factory-Advanced Ring (KEK, Tsukuba).

The sample was a natural antigorite collected from Inner Mongolia, China. Most of the Selected Area Electron Diffraction (SAED) patterns show the presence of the polysomes $m=15$, where m is the number of tetrahedral along a wave (Mellini et al., 1987). Some have $m=16$ and 17. The sample was finely ground and mixed with NaCl, and pressurized in a multi-anvil type high-pressure apparatus (MAX80). Measurements were made at pressures of 0~6 GPa and temperatures of 25~500 C. The pressure was estimated from the compression of NaCl. Diffraction peaks of antigorite were indexed with the aid of indices reported by Uehara and Shirozu (1985) and Capitani and Mellini (2004). Lattice parameters A , a , b , c and β were estimated by the least square method.

The compression in the c -axis dominates the isothermal compression in bulk. The compressibility in the c -axis is larger than those in the a - and b -axes by a factor of ~ 3 . This is consistent with Hilairet et al. (2006). The linear compressibility in the c -axis significantly increases with increasing temperature ($(6\pm 3)\times 10^{-11} \text{ Pa}^{-1}\text{K}^{-1}$), while those in a - and b -axes are almost independent of temperature. The isothermal bulk modulus is estimated to be 60 GPa at room temperature, which is close to the previously reported value.

The expansivity in the c -axis is the largest and largely decreases with increasing pressure, while that in the b -axis the smallest and almost independent of pressure. No significant difference can be seen between axes at the pressure of 5 GPa. The volumetric thermal expansivity is calculated to be $(3.8\pm 0.6)\times 10^{-5} \text{ K}^{-1}$ at $P=0$ GPa, which is consistent with the previous estimation (Holland and Powell, 1998). Our result clearly shows that the expansivity decreases with increasing pressure.

Keywords: equation of state, antigorite, serpentine, compressibility, thermal expansivity

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Microstructure in mullitization from sillimanite

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Transmission electron microscope (TEM) experiments were carried out of sillimanite which was heated in various conditions. The sample taken as starting material was sillimanite crystal in Rudvagssetta, Lutzow-Holm, Antarctica. This starting crystal has no microstructure and l -odd reflections in electron diffractio pattern.

Sample which was heated at 1470C for 1150 hours had two domains by TEM observation; in one domain the reflections with l -odd which is characteristic of sillimanite were obtained in the diffraction pattern, and in another those were not obtained. This In the domain with l -odd reflections, anti-phase boundary (APB) like structure was obaserved. And furthermore, both domains had SiO₂-rich glass inclusions. These relusts indicate that sillimanite decompose to mullite and SiO₂-rich melt/SiO₂-rich amorphous at high temperature. And sillimanite change to disordered sillimanite with mullite components at high temperature and then APB-like structure occures at cooling time.

Keywords: sillimanite, mullite, microstructure

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Experimental study on the phase transition of graphite to hexagonal diamond

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Hexagonal diamond (lonsdaleite) is a metastable polymorph of carbon and occurs as microscopic crystals associated with cubic diamond in some meteorites such as the Canyon Diablo meteorite. Recent theoretical studies reported a possibility that hexagonal diamond has indentation strength and a bulk modulus comparable to or even greater than those of cubic diamond. However, such physical properties of hexagonal diamond have not experimentally investigated due to a difficulty in synthesizing a single-phase bulk sample. Here, we investigated the P-T conditions required to obtain single-phase hexagonal diamond from graphite.

We performed a series of high-pressure and -temperature experiments using a laser-heated diamond anvil cell (DAC) at pressures of 25 and 50 GPa and temperatures ranging from 1400-3300 K. Highly oriented graphite (starting material) was compressed in a DAC without using a pressure transmitting medium and rapidly heated to a target temperature for ~1min using fiber laser. The sample became transparent upon laser heating above 2300 K at 25 GPa and above 1400 K at 50 GPa, suggesting that the phase transition of graphite to diamond phase(s) occurred under those P-T conditions. Interestingly, the transparent area became apparently smaller or almost disappeared (especially in the case of the experiments at 50 GPa) after decompression to room pressure.

The recovered samples were first examined by Raman spectroscopy for phase identification and then by transmission electron microscopy (TEM) for microtextural observations and electron diffraction analysis. The Raman spectra collected from the transparent area in the samples showed a broad peak at 1350-1450 cm^{-1} , but no cubic diamond peak (at 1332 cm^{-1}). TEM observation revealed that the transparent area in each recovered sample consists of hexagonal diamond with a layered structure similar to that of the graphite starting sample. The electron diffraction pattern collected from the sample is complex and can be interpreted as a superposition of three types of reciprocal patterns in which [100], [002] and [-212] of hexagonal diamond are all arranged in a coaxial relation with graphite [002]. This suggests that the martensitic phase transition from graphite to hexagonal diamond proceeds as a result of $1/2a$ or $1/3(1/2)a$ layer shifts of graphene layers along graphite [100].

Keywords: Hexagonal diamond, Highly oriented graphite, Laser-heated diamond anvil cell

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Temperature dependence of XANES spectra for BaTiO₃, SrTiO₃ and TiO₂ with structural phase transitions

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BaTiO₃ is perovskite structure and has good physical properties as industrial material. The main constituent (MgSiO₃CaSiO₃) of the lower mantle is the same structure. Therefore, BaTiO₃ has been intensively studied for a long time. But BaTiO₃ had not been so researched by using X-ray absorption near edge structure (XANES) spectra. XANES spectra of BaTiO₃, SrTiO₃ perovskite and TiO₂ rutile and anatase were measured at various temperatures. The composition, structure and temperature dependence of XANES spectra was investigated especially on the phase transition. The appropriate amount of fine powder sample and boron nitride powder was mixed and pressed into pellet of <0.2 mm thickness and 10.0 mm in diameter. All samples had edge-jumps with 0.7. The measurements of Ti k-edge XANES spectra were carried out in transmission mode at beam line BL-9A of the Photon Factory in KEK, Tsukuba. X-ray absorption measurements in the temperature range from 20K to 800K were made under a helium atmosphere. The XANES spectra for TiO₂ were largely different between anatase and rutile structure, although these two compounds have the same composition. Ti K-edge XANES spectra changed largely with different compositions, while the temperature dependence of XANES spectra is small in each compound even if undergoing structural phase transition. Perovskite-type ATiO₃ compounds reveal several phase transitions. SrTiO₃ and BaTiO₃ perovskite undergo several structural phase transitions in the temperature ranges in this study, SrTiO₃; rhombohedral-tetragonal-cubic, BaTiO₃; trigonal-orthorhombic-tetragonal-cubic, the distinct changing of pre-edge XANES spectra was observed near transition points. Ti atoms are located in TiO₆ octahedral site for the all samples, but Ti k-edge XANES spectra changed largely with different compositions

Keywords: XANES, BaTiO₃, Perovskite, Phase transition